

NanoFASE Deliverable D5.5

REPORT ON THE TRANSFER OF ENM THROUGH REACTORS

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Research Report Summary

In this deliverable, we first describe the behaviour of a 'conservative' nanoparticle type (AuNP) and more reactive NP (Ag and CeO₂ NP) in a pilot waste water treatment plant (WWTP). We show that ENM are removed efficiently by the WWTP regardless of the ENM type and that the release of ENM is mainly governed by the amount of total suspended solids released from the WWTP. The most reactive NP (AgNP) showed considerable variability due to their reaction with sulphide, while the size of less reactive ENM remained relatively constant during the experiment. In the following chapters, we describe the behaviour of ENM during incineration of waste products (i.e. municipal solid waste (MSW) and sewage sludge). We show that nano-CuO and TiO₂ particles experience morphological changes during MSW incineration, namely an increase in particle size, homoaggregation as well as attachment to other ash residues, possibly leading to an immobilisation within the ash. For the incineration of sewage sludge, our pilot scale experiments with reactive ENM reveal that slight differences in the Cu and Zn speciation of sludge spiked with different Cu and Zn forms (nanoparticulate and dissolved) entirely disappear after incineration of the sludge. After incineration, roughly two thirds of the Cu was associated with oxygen, the remaining Cu was coordinated with reduced sulphur. Zn in ash samples was mostly associated with ferrihydrite and to a lesser extent present as ZnAl₂O₄ (gahnite). Furthermore, we demonstrate that CeO₂ NP are nearly quantitatively reduced during sewage sludge incineration, while CeO₂ particles of larger sizes show more resistance towards reduction. In addition, Ce from CeO₂ NP is incorporated into mineral structures, comparable to allanite. This behaviour was also observed in incineration experiments using the sewage sludge generated in the pilot WWTP, containing Au, Ag and CeO₂ NP. Gold NP did not show any significant morphological changes after incineration. Silver NP found within the ash were considerably



lower in size compared to the initial material and still showed partial association with sulphide. Following incineration, we describe the behaviour of inert (AuNP) and reactive ENM (CuO/ZnO as well as AgNP and CeO₂) during pyrolysis, which is a promising alternative treatment option for sewage sludge. We demonstrate that, similar to incineration, the speciation of Cu and Zn is independent of the dosed form (nanoparticulate or dissolved). We show that at pyrolysis temperatures $\geq 600^{\circ}\text{C}$, the content of Zn-S in the char is reduced while concurrently, (weakly crystalline) Zn(-Al) spinel phases are increased. These phases are also present as nanoparticulate concretions within the char, again irrespective of the dosed Zn form. In contrast, no such concretions were observed for the Cu-Fe-S system. At a pyrolysis temperature of 600°C , Ce was distributed across larger aggregates/agglomerates within the char. Silver particles showed partial sulfidation and particle sizes comparable to the initial material. Gold NP found within the char still appeared unaltered. The observed transformation of the reactive ENM during incineration and pyrolysis resulted in a generally low release potential, determined in the following batch leaching and column experiments. However, for AuNP, a considerably higher release potential was observed for the ash, which we attribute to its conservative behaviour during incineration resulting in a far lesser grade of attachment to other ash constituents compared to more reactive ENM.

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September 2019



The NanoFASE project receives funding from the European Union's Horizon 2020 research and innovation programme under grant agreement number 642007. This publication reflects only the authors' view and the Commission is not responsible for any use that may be made of the information it contains.